

QUALITATIVE ANALYSIS

J. O. FRANK

(SECOND EDITION)

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A BRIEF OUTLINE
OF
QUALITATIVE ANALYSIS

*Joseph
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"MANUAL OF QUANTITATIVE CHEMICAL ANALYSIS"
"THE TEACHING OF HIGH SCHOOL CHEMISTRY" ETC.

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INTRODUCTION

(TO FIRST EDITION)

This outline may be used in elementary courses with only occasional reference to the larger texts. However, it will be found applicable with equal facility to the work of the first semester of qualitative analysis of the College or University when used as a supplement to the larger text such as the books of Fresenius, Prescott & Johnson, Treadwell, Noyes, Baskerville & Curtman, F. C. Mathers, Kahlenberg & Walton, Dales & Barneby, etc.

The average student, in trying to use the larger manuals, is constantly losing himself in the maze of directions to the procedures for the analysis of the various groups, sub-groups, etc. To prevent this "getting off the track" and its accompanying waste of chemicals, of time, and energy, the author began about five years ago to use a large chart, which showed in outline an entire scheme of qualitative analysis. It was found that with this chart at hand the student could refer to any number of procedures for separation of the metals, tests for the acid radicals, etc., in fact, to skip about the book or books at will without becoming hopelessly lost or even confused. A demand for this chart from former students and from others who are teaching qualitative analysis has induced me to carefully revise and print it. The outline may be considered an elaboration of the chart itself.

The book should be used where lectures and recitations cover the reactions upon which the various procedures are based. The methods of separating and identifying the metals should be followed by the group and special tests for the acids. As the work proceeds the student should have access to the larger manuals, where the equations representing the various reactions, precautions, special reactions, etc., could be obtained. These points should be taken up during the lecture and recitation periods, together with a clear explanation of the fundamentals of the ionic theory. The student should have considerable practice in writing and balancing the equations representing the various reactions.

When the student is familiar with the separation of the bases and identification of the acids, he is ready for the preliminary tests, and the actual salt analysis. Some instructors prefer to begin the preliminary tests before taking up the identification of the acids.

The methods herein outlined do not attempt to cover the entire subject of qualitative analysis. The separation of the rare metals; salts of the less common acids; fluorides; phosphates and borates of the alkali earth metals; are left for a course in advanced qualitative analysis.

While the work of the lecture and recitation should not be belittled, the best teaching in this subject is that which the instructor does in the laboratory, while the student is engaged in the actual work of identifying the various base and acid constituents of the substance he has been given for analysis.

Teachers may secure a leaflet of suggestions regarding the use of this manual, together with lists of salts to be dispensed, precautions which might well be taken, and other information which has been found helpful in the High Schools, Normal Schools, Colleges, and other schools, where the manual has been used. These leaflets may be obtained free, by teachers, on application to J. O. Frank, Oshkosh, Wis.

J. O. FRANK.

THE METALS

The metals are divided into five groups. These groups receive their names from the reagent used in separating them. If a solution containing salts of all the metals should be made slightly acid with HCl, the chlorides of Hg, Ag and Pb would be precipitated. Thus, Hg, Ag and Pb are classed together as the first, or hydrochloric acid, group. If the filtrate from the above precipitation be treated with an excess of H_2S gas, the metals As, Sb, Sn, Cu, Hg, Pb, Cd and Bi would be precipitated as sulphides. These metals, then, comprise the second or Hydrogen Sulphide group. Likewise the metals of the third and fourth groups are precipitated by $(NH_4)_2S$ and $(NH_4)_2CO_3$, leaving the alkali group in the filtrate.

1. METALS OF THE HYDROCHLORIC ACID GROUP.

Metals which are precipitated from solutions by means of hydrochloric acid.

1. To a solution containing the nitrates of lead, silver and mercurous mercury, add dilute hydrochloric acid with constant stirring until a precipitate ceases to form.

Allow the precipitate to settle and add a few drops of acid to make certain that precipitation has been complete.

Decant the supernatant liquid through the filter, wash the residue twice by decantation and finally transfer it to the filter.

2. Residue.

$PbCl_2$, $AgCl$, $HgCl$.

Treat on the filter with 50 c. c. of boiling water, catching the washings in a beaker and returning to the funnel at least three times.

7. Filtrate.

May contain metals whose chlorides are soluble in dilute hydrochloric acid.

3. Residue.

$AgCl$, $HgCl$.

Stop up the bottom of the funnel by means of a piece of rubber tubing and a pinchcock.

Add NH_4OH until the residue is completely covered. Let stand for five minutes. Remove the pinchcock and catch the filtrate in a beaker.

6. Filtrate.

May contain lead as $PbCl_2$.

1.) To 2 c. c. of the filtrate add a few drops of H_2SO_4 . White precipitate is $PbSO_4$.

2.) To 2 c. c. of the filtrate add 2 c. c. of K_2CrO_4 solution. Yellow precipitate is $PbCrO_4$.

4. Residue.

If black, indicates the presence of Hg.

5. Filtrate.

May contain Ag as $Ag(NH_3)_2Cl$. Acidify with nitric acid. A white precipitate is $AgCl$.

Analyse as in (7), page 4.

THE METALS

II. METALS OF THE HYDROGEN SULPHIDE GROUP.

Metals whose sulphides are precipitated by hydrogen sulphide from solutions of their normal salts, which are slightly acid with hydrochloric acid.

7. To a solution containing normal salts of Antimony, Arsenic, Tin, Copper, Cadmium, Bismuth, Lead and Mercuric Mercury, add enough NH_4OH to make the solution neutral or barely alkaline. Pay no attention to any precipitate that may form.

Add 5 c. c. Con. HCl and dilute to 150 c. c. with water.

Heat nearly to boiling.

Slowly pass H_2S to complete precipitation.

Cool, dilute with one-half its volume of cold water.

Pass H_2S again until a precipitate no longer forms, and then filter.

8. Residue

As_2S_3 , Sb_2S_3 , SnS , SnS_2 , HgS , PbS , Bi_2S_3 , CuS , CdS , and free sulphur.

Y.	O.	Br.	Y.	Bl.	Bl.	Br.	Bl.	Y.	Yellow or white.
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Wash residue with water containing a little H_2S .

Transfer the precipitate to an evaporating dish.

Cover with $(\text{NH}_4)_2\text{S}$, and warm to 75 Deg. C.

Keep warm with constant stirring for five minutes.

Filter.

9. Filtrate.

$(\text{NH}_4)_3\text{AsS}_4$, $(\text{NH}_4)_3\text{SbS}_4$, and $(\text{NH}_4)_2\text{SnS}_3$.

Make barely acid with dilute HCl .

Filter and reject the filtrate.

10. Residue.

As_2S_3 , Sb_2S_3 , SnS_2 and precipitated sulphur.

Punch a hole in the filter and wash the residue into a beaker with a stream from a hot water bottle. Let settle and decant. Treat the moist residue with Con.

HCl . Heat nearly to boiling and keep hot for three minutes. Do not boil.

Dilute with cold water and filter.

11. Residue.

As_2S_3 and sulphur.

Wash free from acid with cold water.

Transfer to an evaporating dish.

Cover with HNO_3 , add 5 c. c. Con. HCl .

Evaporate almost to dryness and take up in a little water.

Filter and reject residue.

Filtrate.

To 5 c. c. of the solution add an equal amount of ammonium molybdate.

Warm for five minutes.

Yellow precipitate indicates arsenic.

Make the remainder of the filtrate alkaline with NH_4OH . Add 10 c. c. of magnesia mixture and let stand. White crystalline precipitate indicates arsenic.

Note. See Baskerville & Curtman on "Marsh's Test" for As.

12. Filtrate.

May contain chlorides of Sb and Sn. Boil five minutes to expel H_2S .

1. Test a portion of the filtrate for Sb by means of the tin couple and a silver coin. A black stain insoluble in a sodium hypochlorite solution indicates antimony.

2. Warm a portion of the filtrate for five minutes with an iron nail and filter into a test tube containing HgCl_2 solution. A gray precipitate indicates the presence of tin.

Prepare a sodium hypochlorite solution by boiling 2 gms. of bleaching powder in 10 c. c. Na_2CO_3 and decanting supernatant liquid.

THE METALS

21. Filtrate.

May contain metals whose sulphides are not precipitated from acid solutions by H_2S .
Analyse as in 21, page 6.

13. Residue.

HgS , PbS , Bi_2S_3 , CuS , CdS .
Wash residue with water.
Transfer to an evaporating dish, and cover with dilute HNO_3 . Boil two minutes.
Dilute. Filter.

14. Residue.

HgS .
To confirm.
Dissolve in Aqua Regia. Evaporate almost to dryness.
Dilute to 10 c. c.
Add 2 c. c. $SnCl_2$ solution. Gray precipitate proves presence of Hg .

Prepare aqua regia just before using as follows:
To one c. c. $Con.$ HNO_3 in a test-tube add 3 c. c. $Con.$ HCl and let stand 5 minutes.

15. Filtrate.

Contains $Pb(NO_3)_2$, $Bi(NO_3)_3$, $Cu(NO_3)_2$, $Cd(NO_3)_2$, and HNO_3 .
Transfer to an evaporating dish
Add 5 c. c. Dil. H_2SO_4 .
Evaporate till white fumes begin to come away.
Cool. Pour into a beaker containing 25 c. c. cold water.
Let stand for ten minutes. Filter.

16. Residue.

$PbSO_4$.
To confirm.
Dissolve in hot ammonium acetate, acidify with acetic acid and add 2 c.c. K_2CrO_4 .
Yellow precipitate is $PbCrO_4$.

17. Filtrate.

$Bi_2(SO_4)_3$, $CuSO_4$, $CdSO_4$.
Make strongly alkaline with NH_4OH .
Filter.

18. Residue.

$Bi(OH)_3$.
Treat on the filter with freshly prepared Na_2SnO_2 .
If residue is changed to a jet black color, Bi is present.

19. Filtrate.

If colorless, contains no copper. Pass H_2S and any cadmium will be precipitated as yellow CdS .

20. If deep blue in color, contains copper.
Add KCN solution until blue color disappears.
Pass H_2S into filtrate.
Yellow precipitate is CdS .

Note. Prepare Na_2SnO_2 by adding $NaOH$ to 1 c. c. of $SnCl_2$, in a test tube, until the first precipitate redissolves.

THE METALS

III. METALS OF THE AMMONIUM SULPHIDE GROUP.

Metals which are precipitated from solutions of their salts by ammonium sulphide.

21. To a solution containing soluble salts of Nickel, Cobalt, Manganese, Zinc, Aluminum, Chromium and Iron, add 2 grams of NH_4Cl and heat to boiling on the hot plate.

Make the solution alkaline with NH_4OH and pass H_2S through the hot solution as long as any further precipitate is produced. Stir for two minutes and filter.

22. Residue.

NiS , CoS , MnS , ZnS , FeS , $\text{Al}(\text{OH})_3$, $\text{Cr}(\text{OH})_3$.

Bl. Bl. Pi. W. Bl. W. Gr.

Wash with hot water containing a little NH_4Cl and H_2S .

Transfer to an evaporating dish and cover with cold HCl (1-10).

Stir for five minutes and filter.

24. Residue.

NiS , CoS , and S .

Wash well with cold water and test with the borax bead. A loop of platinum wire is heated to redness and dipped into the powdered borax. The wire and borax is again heated until only a clear, colorless bead remains on the wire. The clear bead is brought into contact with a portion of the residue to be tested and is again heated until complete fusion has taken place. Upon cooling, the characteristic color will be observed in the bead.

Blue indicates cobalt.

Gray indicates nickel.

In case only nickel is found or the test gives a doubtful result, proceed to confirm the result as follows:

Transfer the residue to an evaporating dish.

Add enough water to barely cover the residue.

Add 5 to 10 c. c. of aqua regia.

Boil until the residue is dissolved.

Evaporate just to dryness and take up in dilute HCl .

Filter and divide filtrate into two parts.

26. For cobalt.

Make the solution barely alkaline with NaOH .

Acidify with acetic acid.

Heat to boiling.

Add 2 grams solid KCl .

Add 5 grams solid KNO_3 .

Warm and shake until the nitrite is dissolved.

Let stand for two hours.

Yellow precipitate indicates the presence of cobalt.

27. For nickel.

Neutralize with NaOH .

Add HCl to bare acidity.

Add KCN until the first precipitate just redissolves.

Make strongly alkaline with a concentrated NaOH solution.

Heat to boiling.

Filter while hot, allowing the filtrate to drop into a test tube containing strong bromine water.

A black precipitate indicates the presence of nickel.

THE METALS

23. Filtrate.

May contain metals which are not precipitated by H_2S .
Make acid at once with acetic acid. Boil until all H_2S is expelled.
Filter and analyse filtrate as directed in 34.

25. Filtrate.

May contain chlorides of Al, Cr, Mn, Zn and Fe, with an excess of HCl.
Evaporate almost to dryness to expel the excess of acid.
Cool and add 20 c. c. strong NaOH.
Add two grams Na_2O_2 and bring to boiling.
Add 2 grams Na_2CO_3 and boil again.
Dilute to twice its volume and filter.

28. Residue.

$Mn(OH)_2$
and $Fe(OH)_3$.

Borax bead
test gives
amethyst color
for Mn.

Sodium car-
bonate and
 $KClO_3$ bead
gives a green
color for Mn.

Dissolve a por-
tion of the
residue in HCl
and add a few
drops of KCNS
solution.

A blood-red
coloration
proves the
presence of
iron.

29. Filtrate.

May contain Na_3AlO_3 , Na_2CrO_4 and Na_2ZnO_2 .
Make barely acid with HNO_3 .
Then barely alkaline with NH_4OH .
Add one gram NH_4Cl and heat to boiling.
Let stand one or two minutes and filter.

30. Residue.

$Al(OH)_3$.
Test on char-
coal with
 Na_2CO_3 ,
 $Co(NO_3)_2$ and
the blow-pipe.
Blue color-
ation indi-
cates Al.

31. Filtrate.

May contain $(NH_4)_2CrO_4$ and
 $Zn(NH_3)_4Cl_2$.
(If yellow, chromium is present.)
Make acid with acetic acid and
divide into two portions.

32. Pass H_2S
through the
solution and
allow to stand
for five min-
utes. White
precipitate in-
dicates pres-
ence of zinc.

33. Add 2 c. c. of
 $Pb(C_2H_3O_2)_2$.
A yellow pre-
cipitate proves
presence of Cr.

THE METALS

IV. METALS OF THE AMMONIUM CARBONATE GROUP.

Metals whose carbonates are precipitated from alkaline solutions of their salts by ammonium carbonate.

34. To a solution containing soluble salts of Barium, Strontium and Calcium, add two grams of NH_4Cl and make alkaline with NH_4OH . Add $(\text{NH}_4)_2\text{CO}_3$ solution to complete precipitation. Heat the solution, keep hot for three minutes, and filter.

35. Residue. BaCO_3, SrCO_3, CaCO_3. Wash residue with water. Punch a hole in the filter paper and wash residue into a beaker with the smallest possible amount of dilute acetic acid. Warm until the residue is dissolved, adding more acetic acid if necessary. Dilute to 50 c. c. and heat to boiling. Add K_2CrO_4 just to complete precipitation. Let settle for five minutes and decant the filtrate through a double filter.		36. Filtrate. May contain Mg and the alkali metals. a.) To a small portion in a test tube add a few drops of $(\text{NH}_4)_2\text{SO}_4$ and $(\text{NH}_4)_2\text{C}_2\text{O}_4$ and filter. Reject residue and test filtrate for Mg as follows: Make alkaline with NH_4OH and add $\text{NaNH}_2\text{HPO}_4$. Rub sides of test tube vigorously with a stirring rod. Crystalline precipitate indicates presence of Mg. b.) Test solution for Na and K as outlined in 44.
37. Residue. BaCrO_4. Proof of Ba. To confirm. Dissolve in HCl and add H_2SO_4.	38. Filtrate. May contain the acetates of Sr. and Ca. Make alkaline with NH_4OH and add $(\text{NH}_4)_2\text{CO}_3$ to complete precipitation. Filter and wash residue with water.	
A white precipitate indicates the presence of Barium.	39. Residue. May be SrCO_3, CaCO_3. Dissolve residue in hot dilute acetic acid. Test a small portion for Sr by shaking vigorously with a little CaSO_4 solution for five minutes. A residue indicates Strontium. Confirm by flame test. 40. a) Strontium is not present. Make the solution alkaline with NH_4OH and add 10 c. c. $(\text{NH}_4)_2\text{C}_2\text{O}_4$ solution. A white precipitate, insoluble in acetic acid, indicates presence of Calcium. 41. b) Strontium is present. Make solution alkaline with NH_4OH and add 10 c. c. $(\text{NH}_4)_2\text{SO}_4$ solution. Boil for five minutes and filter.	Filtrate. Reject.
	42. Residue. SrSO_4. Test with spectroscope or make flame test.	43. Filtrate May contain Ca. Test with $(\text{NH}_4)_2\text{C}_2\text{O}_4$ as outlined above.

THE METALS

V. METALS OF THE ALKALI GROUP.

Metals whose chlorides, sulphides and carbonates are soluble in water.

44. To 2 c. c. of a solution which may contain ammonium, sodium and potassium, add 2 c. c. of NaOH and warm gently.

If ammonium salts are present, ammonia gas will be liberated and may be identified by its odor.

a.) If ammonium salts are not present, test for Na and K with the spectroscope or else make flame tests. A yellow flame, persisting for considerable time, indicates Na. A purple flame indicates K. If K is found, acidify the solution with acetic acid and filter if necessary. To the filtrate add five drops of sodium cobaltinitrite solution. A yellow precipitate on standing indicates the presence of potassium.

b.) If ammonium salts are present they must be removed before the tests can be made for Na and K, as positive results will be obtained whether these metals are present or not. Transfer the solution to an evaporating dish and evaporate to complete dryness.

Continue to heat the dish until all white fumes cease to come away, being careful to heat the sides of the dish as well as the bottom of it. Cool and dissolve a very small portion of the residue in concentrated HCl. Use this for flame and spectroscopic tests. Dissolve the remainder of the residue in water and test for potassium, as outlined in 44(a) above.

Note. It will never be necessary to test for ammonium salts in the filtrate from the ammonium carbonate group, for it is plain that ammonium salts are always present. The analysis of this filtrate is carried out as outlined in 44(b).

In all cases where a solution is to be analyzed for its metal content, the first operation should be to test it for the presence of the ammonium radical. This is done either as outlined above with NaOH or by grinding a portion of the solution with a little slaked lime in a mortar. In both cases the ammonia will be identified by its odor.

General Outline of All the Groups.

45. The solution may contain any of the common metals.

Test for the ammonium radical.

Test for ferrous and ferric iron.

Acidify with HCl.

Residue, HCl group. Analyse as di- rected in 2, page 3.	Filtrate. Pass H_2S to complete precipitation.	
	Residue. Analyse as directed in 8, page 4.	Filtrate. Make alkaline with NH_4OH and pass H_2S to complete precipitation.
		Residue. Analyse as directed in 22, page 6.
		Filtrate. Expel H_2S and add $(NH_4)_2CO_3$ to complete precipitation.
		Residue. Analyse as in 35, page 8.
		Filtrate. Is alkali group.

NOTES ON THE SEPARATION AND IDENTIFICATION OF THE METALS.

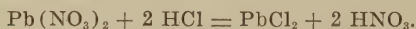
The following notes are numbered to correspond with the numbers which identify the various residues and filtrates in the directions for the separation of the metals.

In case the student has to leave his work unfinished over night or for any period of time he will find it very convenient to label his beaker or funnel containing the residue and number it with the number corresponding to the filtrate or residue in the book. He will thus be certain to begin his work at the proper place upon returning to the laboratory.

I. METALS WHOSE CHLORIDES ARE INSOLUBLE IN WATER AND DILUTE HCl.

1. a. When HCl is added to a solution containing the soluble salts of Pb, Ag or Hg in water, these metals are precipitates as **chlorides**.
- b. The chloride of lead is slightly soluble in **cold** water and very soluble in **hot** water, so that, as a general rule, some of the lead will remain unprecipitated, even in the presence of an excess of HCl, and will be found in the filtrate later.
- c. Dilute HCl will sometimes precipitate the white oxychlorides of Bi or Sb, when these elements are present in large amount. It is well, therefore, to test the precipitated chlorides with a little Con. HCl, which will dissolve the oxychlorides of Sb or Bi, but will not affect the chlorides of Pb, Ag or Hg.

Equations:

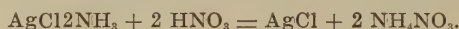


2. a. Lead chloride is very soluble in hot water while silver and mercury chlorides are almost insoluble. The hot water thus affords an easy means of separating and removing the lead chloride. This separation cannot be accomplished by simply pouring the hot water over the precipitated chlorides, but the operation must be repeated at least three times and a considerable quantity of **boiling hot** water must be used.
3. a. When ammonium hydroxide is brought into contact with the chlorides of mercury and silver, a double reaction takes place. The AgCl is changed to the soluble compound AgCl_2NH_3 , while the HgCl is converted into a mixture of black finely divided metallic mercury and the complex $\text{Hg}, \text{NH}_2, \text{Cl}$.
- b. The solution of the AgCl is but slowly brought about and so the ammonium hydroxide is allowed to stand in contact with the AgCl for five minutes or more, after which it is allowed to run through the filter and is caught and tested for silver in the filtrate.
- c. The presence of HgCl is indicated by the instant blackening of the residue when the ammonium hydroxide is added. Ammonium hydroxide instantly reduces HgCl to metallic mercury and the complex mentioned above.

Equations:



5. a. In the presence of **an excess** of HNO_3 the silver ammonium complex is decomposed, yielding again the insoluble silver chloride.



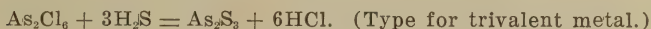
THE METALS

6. a. Lead chloride in hot water solution reacts with sulphuric acid to produce white insoluble lead sulphate. Lead chloride reacts with potassium chromate to produce brilliant canary yellow lead chromate.

II. METALS WHICH ARE PRECIPITATED AS SULPHIDES IN THE PRESENCE OF HCl.

7. a. The solution must be free from nitric acid and other oxidising agents, as these destroy the hydrogen sulphide gas and prevent the precipitation of the sulphides. In the presence of nitric acid the hydrogen sulphide gas produces a white or yellow precipitate of milk sulphur. The nitric acid can be removed by evaporating the liquid to small volume and boiling with five cubic centimeters of concentrated HCl until chlorine ceases to come away.
- b. For the precipitation of arsenic as the sulphide, an acid concentration of one part of concentrated HCl to ten of the solution is best. The solution must also be boiling hot.
- c. The hydrogen sulphide gas should be bubbled **slowly** through the solution. (One bubble a second.) The H_2S ionizes rather slowly, and passing the gas rapidly, simply wastes it.
- d. For the best precipitation of Cadmium as the sulphide, the solution must be cold and weakly acid. When the solution has been cooled and diluted, the hydrogen sulphide should be passed very slowly and the solution allowed to stand for several minutes before filtering.
- e. The filtrate should be further diluted and tested with hydrogen sulphide for traces of the elements of this group. This is absolutely necessary if the filtrate is to be treated later for members of the next group. If the metals of the hydrogen sulphide group are not completely removed, they will cause much trouble in the analysis of the next group.
8. a. From the color of the precipitated sulphides and the order of their precipitation, it is often possible to tell the content of the precipitate. The sulphide of Arsenic is yellow; of Antimony orange; of Tin brown (Stannous) or light yellow (Stannic); of Mercury black; of Lead black; of Bismuth brown; of Copper black; of Cadmium yellow.
- b. It sometimes happens that a trace of nitric acid is present so that the hydrogen sulphide is partially decomposed, yielding a precipitate of free sulphur.

Equations:

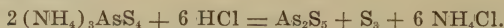


- c. Ammonium poly-sulphide (yellow ammonium sulphide) has the power to convert the sulphides of arsenic, antimony and tin into the corresponding ammonium complexes, which are soluble. This reaction serves as a means of separating As, Sb and Sn from the other members of the group. The ammonium poly-sulphide must be warm but not hot.
- d. Care must be taken not to boil the yellow ammonium sulphide solution, as the CdS and part of the CuS would be dissolved.

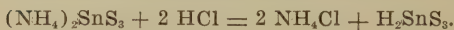
THE METALS

9. The soluble complexes formed by the action of the ammonium poly-sulphide on the sulphides of the metals mentioned above are decomposed by an excess of dilute HCl and the sulphides of the metals are reprecipitated.

Equations:

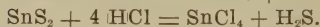


(Type for As and Sb.)



10. a. The precipitation of the sulphides of As, Sb and Sn from a solution of their ammonium sulphide complexes is always accompanied by the precipitation of free sulphur so that the color of the residue does not always show clearly what metals are present.
- b. The precipitated sulphides are washed with water until the wash water is no longer alkaline in order to remove the last traces of the filtrate, which may contain small amounts of Cd and Cu.
- c. In separating the Sn and Sb from the As, advantage is taken of the fact that As_2S_5 is insoluble in hot concentrated HCl while Sb_2S_3 and SnS_2 are easily changed to the soluble chlorides by it.

Equations:



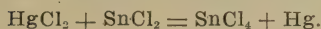
11. a. Although Arsenic sulphide is not soluble in hot HCl, it easily dissolves in aqua regia or HCl and KClO_3 . When the solution has been evaporated to a very small volume, arsenic chloride is produced.
- b. Arsenic chloride reacts with magnesia mixture to produce a white precipitate of Ammonium magnesium arsenate, and with ammonium molybdate to produce yellow ammonium arseno-molybdate.
12. a. The filtrate from 10 above contains the chlorides of Sb and Sn, together with some hydrogen sulphide in solution. By boiling to a low volume the solution of the chlorides is concentrated and all of the hydrogen sulphide removed.
- b. If a concentrated solution of antimony chloride be brought into contact with silver or platinum in the presence of metallic tin, the tin and the silver act as a couple producing a current from the tin to the silver and carrying the ions of antimony with it, thus plating metallic antimony out upon the silver. As arsenic would also plate out under similar circumstances, it is necessary to test the plate of metal with sodium hypochlorite solution. The arsenic is soluble, the antimony insoluble.
- c. The tin couple is simply a semi-circular piece of tin, a half inch in diameter.
- d. The solution of the chlorides of antimony and tin as formed in 10 above contain the tin as Stannic chloride, which is not easily identified. Stannic chloride can easily be reduced to stannous chloride by the action of nascent hydrogen produced when the acid, which is also present in the solution, comes into contact with metallic iron, which can be introduced in the form of a nail or a pair of iron tweezers. The stannous chloride reacts readily with mercuric chloride, producing a precipitate which is generally of a white silky character, though under certain conditions it may be gray or even black. The variation in color of the precipitate produced is due to a variation in the relative amounts of the reacting compounds.

THE METALS

Thus: Where a large amount of HgCl_2 is added to a comparatively small amount of SnCl_2 , the following reaction takes place and white HgCl is produced.



But: Where only a few drops of the HgCl_2 solution are added to a fairly concentrated solution of the SnCl_2 , a complete reduction of the HgCl_2 to metallic mercury is produced.



13. a. It is necessary to wash the remaining sulphides of the metals of this group until the wash water no longer gives an alkaline reaction. This will remove traces of the Arsenic, Antimony and Tin complexes, which might give trouble if allowed to remain in the residue.
b. In treating this residue with nitric acid to effect a separation of the mercury sulphide, advantage is taken of its insolubility in cold dilute nitric acid, all of the sulphides of the other metals being converted to the soluble nitrates by this treatment.
14. a. The black residue of HgS may be converted to HgCl_2 by dissolving in aqua regia and evaporating to small volume to remove the excess of nitric acid and chlorine. If this solution be diluted and treated with stannous chloride solution, the same result will be obtained as in the detection of tin in 12.
b. A white residue is S.
15. a. The solution containing the nitrates of Cu, Cd, Bi, and Pb, together with a small amount of nitric acid, is treated with a small amount of sulphuric acid and the solution evaporated to a small volume. This treatment changes the nitrates of the metals to the corresponding sulphates and if carried far enough also removes the nitric acid produced by the reaction.
b. The sulphates of Cu, Cd, and Bi are soluble in water, whereas the sulphate of lead is almost entirely insoluble in cold dilute sulphuric acid solution. This treatment then causes the lead to precipitate from the solution, leaving the Cu, Cd, and Bi as sulphates in the filtrate.
16. Lead sulphate is soluble in hot ammonium acetate solution, and is converted thereby to lead acetate, which reacts readily with potassium or sodium chromate to produce yellow lead chromate, which is easily recognized.
17. If a solution of the soluble sulphates of Cu, Cd, and Bi be treated with enough ammonium hydroxide to make the solution alkaline, a precipitate of the hydroxides of these metals would be produced. If, however, enough ammonium hydroxide be added to make the solution **strongly** alkaline, the hydroxide of cadmium redissolves to form a colorless solution and the hydroxide of copper redissolves to form a solution in which the slightest traces of copper gives a **deep blue** color. Since the hydroxides of both Cadmium and Copper redissolve, the hydroxide of Bismuth alone remains as a precipitate.
18. Bismuth hydroxide is a white insoluble compound which is easily reduced to black metallic bismuth by the action of any strong reducing agent. Potassium or sodium stannite is generally used. In identifying bismuth hydroxide, the substance must be wet, but not covered with water, and the sodium stannite must be concentrated.

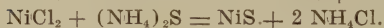
THE METALS

19. Since Copper Hydroxide in an ammoniacal solution is blue, a colorless solution at this point would indicate the absence of copper, in which case the cadmium could be detected by simply passing hydrogen sulphide through the solution and noting the yellow sulphide which will be formed if cadmium is present.
20. If copper hydroxide is present in the solution and hydrogen sulphide is passed, the copper sulphide formed (black) would obscure the appearance of the yellow cadmium sulphide. If KCN solution is added in excess, both the cadmium and the copper form soluble **colorless** double cyanides. The copper cyanide solution is not decomposed by hydrogen sulphide, while the cadmium cyanide is easily broken up to form the yellow cadmium sulphide.

THE AMMONIUM SULPHIDE GROUP.

21. The metals of the ammonium sulphide group are not precipitated by hydrochloric acid nor by hydrogen sulphide from solutions containing an appreciable amount of free hydrochloric acid. They are, however, easily precipitated by ammonium sulphide from a solution which has previously been made alkaline with ammonium hydroxide, or by hydrogen sulphide from a solution which is alkaline with ammonium hydroxide and which contains ammonium chloride.
- a. With solutions which are known to be free from metals of the first two groups, the metals aluminum, chromium and iron may be precipitated by ammonium hydroxide, as a preliminary test before the addition of the ammonium sulphide. In this case the solution should be made barely alkaline with ammonium hydroxide and five grams of ammonium chloride added to insure the complete precipitation of the hydroxides of aluminum and iron. The solution should be boiled until the odor of ammonia is very faint, as this insures the precipitation of the last traces of the Al and Fe. The color of the hydroxides would indicate which metals were present. Ferric hydroxide is brown; aluminum hydroxide white and flocculent; chromium hydroxide apple green or light blue. If no precipitate is produced with ammonium hydroxide, no Al, Cr, or Fe is present.
- b. After the solution has been made alkaline with ammonium hydroxide in the manner mentioned in (a) and a careful note made as to the presence or absence of the metals Al, Cr, and Fe, the solution should be brought to boiling and a slow stream of hydrogen sulphide passed (or ammonium mono-sulphide added). This will precipitate the nickel, cobalt, manganese and zinc as sulphides and will at the same time react with the iron hydroxide, changing much of it to iron sulphide. The color of the precipitated sulphides often indicates which metals are present. Cobalt, nickel and iron sulphides are all jet black; manganese sulphide is pink; zinc sulphide is white.

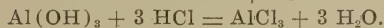
Equations: (Typical)



THE METALS

- c. It must be remembered that when the solution has already been treated for the first two groups, hydrogen sulphide is present and unless removed by boiling will cause the precipitation of the sulphides of the metals of this group as soon as the solution is made alkaline.
22. a. The precipitate of mixed sulphides and hydroxides should be carefully washed to free it from any metals of the succeeding groups. The wash water should contain ammonium chloride and hydrogen sulphide to prevent the formation of colloidal sulphides, which would be carried through the filter as a white, milky precipitate by the wash water.
- b. The separation of the nickel and cobalt from the other metals of the group depends upon the fact that the sulphides of nickel and cobalt are insoluble in Dil. HCl (1-10) whereas all the other sulphides and hydroxides which might be present are easily dissolved.

Equations: (Typical)

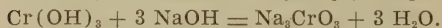
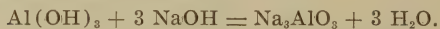


24. a. The residue of NiS and CoS should be jet black or black with a trace of yellow or white precipitated sulphur from the decomposition of the other sulphides. If it contains no trace of black compounds, it cannot contain NiS or CoS.
- b. Care should be taken in making the borax bead test that the bead be perfectly colorless before any of the sulphide is taken up. Many borax bead tests fail because the bead is not properly prepared or because the mixture was not made hot enough after the metal was taken up by the bead.
- c. The deep blue of the cobalt may obscure the gray of the nickel if both are present, but the nickel will never obscure the cobalt even though only a trace of this metal be present. If a pure deep blue color be obtained, only cobalt is present, while a gray or grayish brown color uncolored with the slightest trace of blue would indicate the presence of nickel only. When only one metal is present, the borax bead test is sufficient and no further identification is needed.
- d. Where the borax bead test is not conclusive or where both Ni and Co appear to be present, it is well to verify the tests by the wet method.
- e. When a substance has been dissolved in a strong acid it is generally necessary to expel the excess of acid, after the solid is in solution, by evaporating the liquid to dryness and then dissolving the residue in water or a small amount of dilute acid.
26. a. If any cobalt chloride is present, the NaOH will precipitate it as Cobalt Hydroxide. This hydroxide is easily soluble in acetic acid, forming Cobalt acetate. In the presence of an excess of potassium nitrite and potassium chloride, cobalt acetate is easily converted to the yellow-crystalline potassium cobalti-nitrite.
27. a. If nickel chloride is present, a greenish precipitate will be produced by sodium hydroxide. This nickel hydroxide is soluble in hydrochloric acid, producing the green nickel chloride, which unites with a small amount of KCN to produce insoluble nickel cyanide, which redissolves in an excess of KCN, forming the double cyanide of nickel and potassium. This double cyanide is easily decomposed by the sodium hypobromite produced when NaOH is saturated with bromine water, producing black $\text{Ni}(\text{OH})_2$.

THE METALS

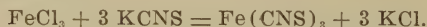
25. a. Whenever a solution is strongly acid and is to be made strongly alkaline, it is well to expel the excess of acid by evaporation before adding the alkali, as this prevents the saturation of the solution by salts of the alkali metals, and better results will be obtained in every way.
- b. The sodium peroxide acts as a strong oxidising agent and converts the chromium and zinc salts to the soluble chromates and zincates. (The aluminum salts were converted to the soluble aluminates by the NaOH.)

Equations: (Typical)



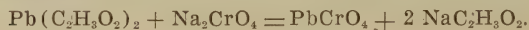
- c. The hydroxides of iron and manganese are precipitated when the solution is made strongly alkaline with NaOH, but unlike the aluminum and zinc hydroxides, they are not soluble in an excess of NaOH. Both are affected by the sodium peroxide, however, the manganese hydrate being changed to manganese dioxide and the ferrous hydrate to ferric hydrate.
- d. The solution is finally boiled with a little sodium carbonate to effect the decomposition of the excess of sodium peroxide.
28. a. Ferric hydroxide dissolves in HCl to form ferric chloride which reacts with KCNS to form blood red iron sulpho cyanate.

Equation:



29. a. When the solution is made acid with nitric acid, the sodium aluminate and sodium zincate are decomposed, being changed to the corresponding nitrates. The sodium chromate is not decomposed in a bare excess of nitric acid, though it may be changed to the red bichromate in an excess of the acid.
- b. When ammonium hydroxide is added to the solution which is barely acid with nitric acid, white aluminum hydroxide is precipitated. The zinc remains in solution as an ammonium complex. The chromate, which may be identified by its yellow color, is unaffected by the ammonium hydroxide.
30. When aluminum hydroxide is heated on charcoal in the presence of cobaltus nitrate, blue cobalt aluminate is formed.
32. Hydrogen sulphide precipitates zinc as zinc sulphide from solutions of zinc salts which have been slightly acidified with acetic acid.
33. Lead acetate precipitates yellow lead chromate from solutions of soluble chromates.

Equation:



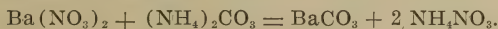
IV. THE AMMONIUM CARBONATE GROUP.

34. The metals of the ammonium carbonate group are not precipitated by HCl, nor by Hydrogen Sulphide in either acid or alkaline solution, nor by Ammonium Hydroxide. They are precipitated by Ammonium Carbonate in the presence of Ammonium Chloride.
- a. If the solution is known to contain Hydrogen Sulphide, it should be boiled to expel this gas before testing for the alkaline earth metals.

THE METALS

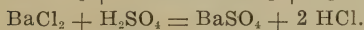
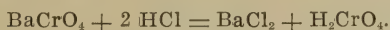
- b. If the solution is known to be free from the metals of the preceding groups and from Hydrogen Sulphide, no boiling is necessary and it may be made alkaline with ammonium hydroxide (unless it is already alkaline), a few grams of solid ammonium chloride added and the metals precipitated by the addition of a slight excess of ammonium carbonate solution.

Equation: (Typical)



35. a. The precipitated carbonates are washed with water to remove traces of the filtrate which may contain Mg, Na, or K.
 b. The carbonates are dissolved in acetic acid and the solution boiled strongly to remove the last traces of carbon dioxide, which might interfere with the strontium test if not removed.
 c. The solution is heated to boiling to insure a granular precipitate when the potassium chromate is added.
37. Barium chromate is a canary yellow compound easily soluble in hydrochloric acid, yielding barium chloride, which reacts with sulphuric acid to give white insoluble barium sulphate. The yellow precipitate is generally sufficient evidence of barium.

Equations:



38. The strontium and calcium are precipitated again as carbonates in order to separate these metals from the potassium chromate which was added to precipitate the barium and which would interfere with the strontium test in a concentrated solution.
39. Since calcium sulphate is less soluble than strontium sulphate, a saturated solution of calcium sulphate would cause the precipitation of strontium sulphate. The reaction is best brought about by boiling the solution or shaking vigorously for several minutes. On standing, the strontium sulphate will settle as a very fine white granular precipitate. Strontium salts give a red flame coloration.
40. Ammonium oxalate precipitates white calcium oxalate from alkaline solutions of calcium salts. The solution must be known to be free from strontium and barium if the test is to be certain.
41. When a test on a small portion of the solution (39) shows the presence of strontium, this metal may be almost completely removed by precipitation with ammonium sulphate in alkaline solution. The precipitation is complete if the solution be concentrated and if two or three fresh portions of ammonium sulphate be added to the boiling hot solution at intervals of one or two minutes.
43. Ammonium oxalate precipitates white insoluble calcium oxalate from alkaline solutions of calcium salts. Sr and Ba must be known to be absent, as their salts also give a precipitate with ammonium oxalate.

Equation:



V. METALS OF THE ALKALI GROUP.

36. Magnesium is in many respects one of the metals of the alkali group. It is not precipitated by ammonium carbonate unless ammonium salts are absent, which is rarely the case after the removal of metals of the preceding groups.
 - a. Since di-sodium phosphate gives a precipitate with salts of Ba, Sr, and Ca, these metals must be known to be absent before a reliable test for Mg can be made. When the last traces of the alkaline earth metals have been removed by treatment with ammonium sulphate and ammonium oxalate, di-sodium hydrogen phosphate may be used as a test for magnesium. Sodium ammonium phosphate may also be used.
44.
 - a. Ammonium salts may always be identified by treatment with NaOH, KOH, or Lime and heating gently, as they invariably yield free ammonia when so treated. Since ammonium salts interfere with the tests for sodium and potassium, it is always necessary to remove them before the tests for sodium or potassium can be made.
 - b. If ammonium salts are shown to be present in a solution to be tested for Na or K, evaporate the solution to dryness and heat the residue until the last traces of white fumes have ceased to come away. Cool the dish and take up the residue in distilled water. The salts of ammonium are all volatile and are completely removed from the solution by the above treatment.
 - c. Since nearly all salts contain traces of Na, the flame test for this metal is never very certain unless all other metals are known to be absent.
 - d. The flame test for K is very reliable when carefully made, but as in the case of Sr, Ba, and Na, the spectroscope gives most accurate results.

THE ACIDS

THE ACIDS

The acids are divided into three groups:

GROUP I.

The sulphuric acid group, consisting of Sulphuric, Sulphurous, Thiosulphuric, Chromic, Arsenious, Arsenic, Phosphoric, Boric, Silicic, Tartaric, Carbonic and Oxalic Acids. Barium chloride precipitates the barium salt of each of these acids from neutral solutions of any of the alkali salts of the acids.

GROUP II.

The hydrochloric acid group, consisting of Hydrochloric, Hydrobromic, Hydriotic, Hydrocyanic, Sulphocyanic, Hydroferrocyanic, Hydroferricyanic, and Hydrosulphuric. Silver nitrate precipitates the silver salt of each of these acids from nitric acid solutions of their alkali salts.

GROUP III.

The nitric acid group, consisting of Nitric, Nitrous, Chloric, and Acetic Acids. Solutions of salts of these acids give no precipitate from neutral solutions with barium chloride nor from nitric acid solutions with silver nitrate.

Group Tests for the Acids.

Sodium, Ammonium and Potassium salts may be tested directly for their acid radicals. Salts of all other metals are treated with sodium carbonate to remove the base. The filtrate, now known as the **prepared solution**, is examined for the acids as follows:

46. A. Barely acidify **one-half** of the solution with HNO_3 , discard any precipitate. Boil five minutes to expel CO_2 . Make barely alkaline with NH_4OH and boil until the odor of ammonia can no longer be detected. (Solution is now considered neutral.) Divide into two parts.
 1. Add 5 c. c. BaCl_2 solution. Boil strongly. Precipitate indicates presence of first group acid. Test solubility of the precipitate in HCl .
 - a. Precipitate is insoluble, indicates a **sulphate**.
 - b. Precipitate is soluble, indicates a first group acid other than sulphuric. Make special acid tests on the prepared solution to determine which acids are present.
 2. Make acid with HNO_3 . Add 5 c. c. AgNO_3 . A precipitate proves presence of second group acid.
 - a. Precipitate is insoluble in NH_4OH . May indicate a Ferrocyanide or Iodide.
 - b. Precipitate is soluble in NH_4OH . May be any acid of second group other than Ferrocyanide or Iodide. Make special acid tests on the prepared solution to determine which acids are present.
- B. In case no acids of groups 1 or 2 are found, make the special tests for the acids of group 3.

Note. Where more than one acid is found and one of them is shown to be in group 1, a fresh portion of the prepared solution must be treated with Barium Nitrate to precipitate the acids of group 1 and the filtrate tested for acids of groups 2 and 3. The student must remember that he has added barium nitrate and so should not make the test for nitric acid.

THE ACIDS

FIRST GROUP ACIDS.

Sulphuric acid (Sulphates).

47. Barium chloride precipitates from solutions of sulphates, white barium sulphate which is insoluble in hot hydrochloric acid.

Sulphurous acid (Sulphites)

48. Barium chloride precipitates from solutions of soluble sulphites white barium sulphite which is easily soluble in dilute hydrochloric acid.
49. Sulphites when heated gently with concentrated sulphuric acid evolve sulphur dioxide fumes and (unlike thiosulphates) leave a clear solution.
50. Lead acetate precipitates from a soluble sulphite solution, lead sulphite. This is soluble in nitric acid and (unlike thiosulphates) does not blacken on boiling.

Thiosulphuric acid (Thiosulphates)

51. Barium chloride precipitates from solutions of soluble thiosulphates, barium thiosulphate which is soluble in hydrochloric acid, leaving a residue of sulphur. Calcium chloride gives no precipitate with a soluble thiosulphate. (Unlike sulphites.)
52. Upon heating a thiosulphate gently with concentrated sulphuric acid, sulphur dioxide fumes are given off, leaving a residue of free sulphur.
53. Lead acetate gives with soluble thiosulphates a white precipitate of lead thiosulphate, which blackens on boiling.

Oxalic acid (Oxalates)

54. Barium chloride precipitates from neutral solutions of soluble oxalates, white barium oxalate which is easily soluble in sulphuric acid, yielding a solution of oxalic acid which easily decolorizes a dilute solution of potassium permanganate.
55. Upon heating an oxalate in a closed tube it is blackened or charred.
56. Oxalates when heated with concentrated sulphuric acid yield carbon dioxide.
57. Oxalates when dissolved in dilute sulphuric acid yield oxalic acid which decolorizes a dilute potassium permanganate solution.
58. Calcium chloride or calcium hydroxide precipitates from solutions of soluble oxalates, white calcium oxalate which is insoluble in acetic acid.

Carbonic acid (Carbonates)

59. Most carbonates when heated in a closed tube are decomposed, yielding carbon dioxide.
60. Upon heating carbonates with dilute HCl or H_2SO_4 , carbon dioxide is evolved which precipitates white barium carbonate from a barium hydroxide solution.
61. Sodium carbonate precipitates magnesium carbonate from a solution of magnesium sulphate, while sodium bicarbonate does not.

Tartaric acid (Tartrates)

62. Tartrates are charred upon heating in a test tube, yielding the odor of burnt sugar.
63. Calcium chloride precipitates from solutions of neutral tartrates, white calcium tartrate which is soluble in hydrochloric and acetic acids.

THE ACIDS

64. Calcium hydroxide precipitates from solutions containing tartrates, white calcium tartrate which is soluble in cold KOH, but which precipitates out as a gelatinous mass when the solution is heated. It re-dissolves as the solution cools.
65. Silver nitrate precipitates from solutions of neutral tartrates, silver tartrate which turns black upon boiling. If the black precipitate thus obtained is washed and dissolved in a little ammonium hydroxide in a clean test tube, a mirror of metallic silver will be formed if the test tube is allowed to stand in a water bath at 100 degrees C. for a few minutes. (See citrates.)

Citric acid (Citrates)

66. Citrates are charred when heated in a test tube.
67. Barium chloride precipitates from neutral solutions of citrates, white barium citrate which is soluble in HCl.
68. An excess of calcium hydroxide produces no precipitate with citric acid or soluble citrates in the cold. In hot solutions a white precipitate of calcium citrate is produced. This precipitate is insoluble in KOH (unlike tartrates), but soluble in acetic acid, (unlike oxalates).
69. Silver nitrate precipitates from neutral solutions of citrates, white silver citrate which does not turn black on boiling (unlike tartrates).

Chromic acid (Chromates)

70. Chromates are generally yellow colored salts which yield the characteristic chromium green when fused with borax.
71. Barium chloride gives with soluble chromates, a precipitate of yellow barium chromate which is soluble in HCl.
72. Lead acetate gives with solution of soluble chromates, yellow lead chromate which is soluble in concentrated KOH.

Arsenic Acid (Arsenates)

73. Barium chloride precipitates from neutral solutions of arsenates, white barium arsenate which is soluble in HCl.
74. Hydrogen sulphide precipitates yellow arsenic sulphide from hot acid solutions.
75. Silver nitrate gives a chocolate-colored precipitate with solutions of arsenates.
76. Arsenate gives a yellow precipitate with ammonium molybdate from hot HNO₃ solution, but this precipitate is not to be relied upon unless phosphoric acid is known to be absent. This precipitate is not given by arsenites.

Arsenious acid (Arsenites)

77. Barium chloride gives a white precipitate of barium arsenite from neutral arsenite solutions.
78. Silver nitrate gives a yellow precipitate from neutral arsenite solutions.
79. Hydrogen sulphide precipitates yellow arsenic sulphide from either hot or cold solutions of arsenites. Arsenates are precipitated only in hot solutions.

Phosphoric acid (Phosphates)

80. Barium chloride precipitates from neutral solutions of phosphates, white barium phosphate which is soluble in HCl.
81. Ammonium molybdate precipitates from nitric acid solutions of phosphates, yellow ammonium phosphomolybdate when warmed gently. (If arsenic in any form is present it must first be removed by precipitation with hydrogen sulphide, as arsenates give a precipitate with ammonium molybdate which is similar to the yellow ammonium phosphomolybdate.)

THE ACIDS

Silicic acid (Silicates)

82. Barium chloride precipitates from solutions of silicates, barium silicate which is sparingly soluble in HCl.
83. A slight excess of HCl precipitates from concentrated solutions of soluble silicates, gelatinous silicic acid.
84. If a small sample of an insoluble silicate be mixed with its own weight of pure calcium fluoride and warmed in a platinum crucible with a little concentrated sulphuric acid, silicon tetra fluoride will be liberated. This gas may be detected by means of a drop of water held on a stirring rod near the edge of the crucible lid. If SiF_4 is coming away from the crucible the drop of water will become turbid, due to the formation of H_2SiO_3 .

Boric acid (Borates)

85. Barium chloride precipitates from solutions of borates, white barium borate which is soluble in HCl.
86. When borates are treated with sulphuric acid, boric acid is produced. If alcohol be added in excess and the mixture ignited, it burns with a green flame.

SECOND GROUP ACIDS.

Hydrochloric acid (Chlorides)

87. Silver nitrate precipitates from nitric acid solutions of chlorides, white silver chloride which is soluble in NH_4OH , but reprecipitated by HNO_3 .
88. Most chlorides are readily decomposed when heated with concentrated sulphuric acid yielding hydrochloric acid gas.
89. If a dry chloride be mixed with powdered potassium bichromate, moistened with concentrated sulphuric acid and distilled from a dry retort, a gas will be produced which, when passed into an ammonium hydroxide solution, gives it a yellow coloration. Bromides and iodides do not interfere with this test.
90. A concentrated solution of a soluble chloride when boiled with MnO_2 and H_2SO_4 yields a stream of free chlorine which has the power to impart a blue coloration to KI starch paste, and which, if allowed to escape into the air in any quantity, may be identified by its odor.

Hydrobromic acid (Bromides)

91. Silver nitrate precipitates from nitric acid solutions of bromides, white silver bromide which is soluble in ammonium hydroxide, but reprecipitated by nitric acid.
92. Bromides when heated with Con. sulphuric acid yield free bromine, which may be identified by its color and odor or by shaking with a little KI solution in the presence of one cubic centimeter of CS_2 .
93. Solutions containing bromides, when slightly acidified by the addition of a drop of dilute sulphuric acid, yield, when a crystal of potassium nitrite is added, free bromine which may be shaken out with a little CS_2 . The bromine will impart a reddish color to the CS_2 . Chlorine water may be used instead of the potassium nitrite.

Hydriotic acid (Iodides)

94. Iodides when warmed with Con. sulphuric acid yield free iodine which comes away as a purple vapor.
95. Silver nitrate precipitates from iodide solutions, pale yellow silver iodide which is almost insoluble in ammonium hydroxide.

THE ACIDS

96. Soluble iodides, when treated with a drop of dilute sulphuric acid and a crystal of potassium nitrite, yield free iodine, which may be shaken out with CS_2 . The iodine will color the CS_2 a deep purple. Chlorine or bromine water may be used instead of the potassium nitrite.

Hydrosulphuric acid (Sulphides)

97. Most sulphides are decomposed upon warming with concentrated acids, yielding hydrogen sulphide which has a characteristic odor and which reacts with lead acetate paper to give black lead sulphide.
98. Silver nitrate precipitates from HNO_3 solutions containing a soluble sulphide or hydrogen sulphide, black silver sulphide.
99. A few sulphides are not decomposed by sulphuric or hydrochloric acids, but are oxidised by aqua regia yielding sulphuric acid which gives an insoluble precipitate with barium chloride.

Hydrocyanic acid (Cyanides)

100. Most cyanides are decomposed by heating, yielding cyanogen which has the odor of peach kernels.
101. Silver nitrate precipitates from a HNO_3 cyanide solution, white silver cyanide which is soluble in ammonium hydroxide.
102. An alkali cyanide solution, when treated with a little NaOH , a few drops of FeCl_3 , a crystal of FeSO_4 , and warmed, will yield a blue precipitate when acidified with HCl . Other cyanogen compounds will interfere with the test.
103. A Dil. ammoniacal CuSO_4 solution is decolorized by an alkali cyanide.

Thiocyanic acid (Thiocyanates)

104. Silver nitrate precipitates from thiocyanate solutions, acidified with HNO_3 , white silver thiocyanate which is soluble in NH_4OH .
105. An alkali thiocyanate, when acidified with HCl and a few drops of ferric chloride are added, yields a blood-red solution of ferric thiocyanate.
106. Thiocyanates are decomposed by fusion with KNO_3 , yielding potassium sulphate, which yields an insoluble precipitate with barium chloride.

Hydroferricyanic acid (Ferricyanides)

107. A ferricyanide solution acidified with HNO_3 yields a reddish-brown precipitate when treated with silver nitrate.
108. If a few drops of freshly prepared ferrous sulphate solution be added to an alkali ferricyanide solution which has been slightly acidified with HCl , a blue precipitate of "Turnbull's Blue" is produced.
109. Insoluble ferricyanides are transposed by boiling with KOH , the filtrate giving a ferricyanide test with ferrous sulphate.

Hydroferrocyanic acid (Ferrocyanides)

110. Silver nitrate precipitates from nitric acid solutions of ferrocyanides, white silver ferrocyanide which is insoluble in ammonium hydroxide.
111. An alkali ferrocyanide when acidified with hydrochloric acid and treated with a few drops of ferric chloride yields a blue precipitate of "Prussian Blue."
112. Insoluble ferrocyanides are transposed by boiling with KOH , the filtrate yielding the ferrocyanide test when treated with ferric chloride.

THE ACIDS

THIRD GROUP ACIDS.

Nitric acid (Nitrates)

113. Nitrates give no precipitate with barium chloride or with silver nitrate in nitric acid solution.
114. Nitrates are decomposed by heating with concentrated sulphuric acid, yielding brown fumes of nitrogen dioxide. (Nitric oxide plus the oxygen of the air.)
115. Soluble nitrates give a characteristic test with ferrous sulphate and concentrated sulphuric acid which is made as follows: Three cubic centimeters of the nitrate solution are mixed in a test tube with one cubic centimeter of a freshly prepared ferrous sulphate solution. The test tube is inclined at an angle of forty-five degrees, and two cubic centimeters of concentrated sulphuric acid are carefully poured into the tube, care being taken that the acid runs to the bottom of the test tube without mixing with the nitrate solution. Upon standing for a few minutes a brown ring will form at the junction of the sulphuric acid and the nitrate solution.
116. (Nitrites also give this test. A nitrite can be distinguished from a nitrate by the fact that a nitrite has the power to release iodine from a potassium iodide solution while a nitrate does not. In this test the nitrite solution should have a trace of free sulphuric acid present.)

Acetic acid (Acetates)

117. Acetates are decomposed when heated, yielding free carbon. In the presence of sulphuric acid, acetic acid is given off which may be known by its odor. (Vinegar.)
118. Acetates give no precipitate with barium chloride nor with silver nitrate in nitric acid solution.
119. If an acetate or its concentrated solution be treated with two cubic centimeters of amyl alcohol and the same amount of concentrated sulphuric acid, the solution will, upon warming, yield amyl acetate, which may be identified by its fruit-like odor.

Chloric acid (Chlorates)

120. Chlorates are decomposed when heated with concentrated sulphuric acid. This decomposition almost always takes place with explosive violence.
121. Chlorates when heated strongly give up their oxygen and become chlorides. The heating must be continued until the residue has become solid. This residue will give a typical chloride test with nitric acid and silver nitrate.

(Other halogen acids would interfere with this test and their absence must be proved before the test is made.)

* * * * *

OXIDES AND HYDROXIDES.

All soluble oxides and hydroxides give an alkaline reaction when dissolved in water. The oxides and hydroxides of the heavy metals are reduced when heated in a combustion tube in a stream of Hydrogen, yielding the free metal. Where the analysis has failed to show the presence of an acid, the reduction test should be made. It should be remembered that the hydroxide when heated yields water and the oxide.

PRELIMINARY EXAMINATION

FOR

METALLIC AND ACID CONSTITUENTS

- A. Note carefully the Physical Appearance of the substance under examination. If it be in a finely divided form a microscope should be used.
- The substance appears to be homogeneous.
Probably a single salt.
 - The substance is not homogeneous.
Probably more than one salt.
 - Note the form in which the substance occurs.
 - A Powder. Most oxides, carbonates and sulphides occur as powders.
 - Crystals. Most sulphates, nitrates and chlorides occur as crystals.
 - Metallic. Note color. Also test with magnet for Ni, Co and Fe.
 - Liquid. Evaporate a portion to dryness and examine residue.
 - Note the color of the substance. If it is colored, make a note of its probable metallic content, from the following:
 - Red. Sb_2S_3 , Cu_2O , Pb_3O_4 , HgO , HgI , Bichromates, and most salts of cobalt and iron are some shade of red or else orange in color.
 - Green. Most salts of nickel and chromium and many salts of copper and iron are green.
 - Blue. Most salts of copper and many salts of cobalt, nickel and iron are blue.
 - Pink. Most salts of manganese and a few of iron are pink.
 - Yellow. PbO , PbI , CdS , As_2S_3 , AgI , nearly all chromates and a few salts of iron are yellow.
 - Black. May be a sulphide of Co, Ni, Cu, Fe, Ag, Hg, Pb or an oxide of Ni, Co, Cu or Ag.
 - Brown PbO_2 , $\text{Mn}(\text{OH})_2$, Bi_2S_3 , SnS_2 and many salts of iron are brown.
 - Note carefully the attitude of the substance toward water and acids.
 - Substance is deliquescent.
May be NaOH , KOH , Ammonium Salts, Alkali Acetates, Nitrites, Nitrates or Chlorides of Ca, Sb, Bi, Zn, etc.
 - The substance is efflorescent.
May be Sulphites, Sulphates, Thiosulphates, etc.
 - The substance is soluble in water.
 - Easily.
 - Only in hot water.
 - In water containing a small amount of acid.
 - Soluble in water containing a trace of acid, but insoluble when diluted. Precipitate is soluble in excess of acid.
 - The substance is insoluble in water. Soluble in acids.
 - Substance is insoluble in water and acids.

STUDY SOLUBILITY TABLE IN APPENDIX.

PRELIMINARY EXAMINATION

B. Examination of a Substance by Heating in a Test Tube.

1. Heat two grams of the substance in a hard glass test tube to the highest temperature the tube will stand and note any change that may take place.
 - a. The substance sublimes.

May be Ammonium or Mercury salt; oxide of arsenic, antimony or zinc; iodine, sulphur or mercury.
 - b. The substance chars.

May be a salt of Oxalic, Tartaric, Acetic, or Citric acids. Make special tests for these acids. Some carbonates and many other organic compounds such as starch, sugar, cellulose, etc., char upon heating. Some sulphides are blackened by heating and a few compounds blacken when sufficient heat is applied to decompose them and yield the finely divided metal.
 - c. The substance changes color.
 1. White to yellow. ZnO , ZnCO_3 , and Sb_2O_3 .
 2. Yellow to black. Sulphur and certain sulphides.
 3. Blue, red, green, pink or brown, changing to black. Salt of Cu, Co, Ni, Mn or Cr.
 4. Yellow to red. Certain chromates.
 5. Red to yellow. HgI .
 - d. Water is given off.

Salts containing water of crystallization, hygroscopic water, hydroxides, some basic salts and many organic compounds give up water upon heating.
 - e. A gas is given off.

Test with glowing splinter. Many oxides and other salts rich in oxygen give up this gas when heated.
2. Cover two grams of the substance with a small amount of concentrated sulphuric acid and gently warm in a test tube.
 - a. A colored gas is given off. Note color, odor, combustibility, etc.

A brown gas, NO_2 , indicates Nitrate or Nitrite.
A brown gas, Br, indicates Bromide.
A yellowish-green gas, Cl, indicates Hypochlorites.
A purple gas, I, indicates Iodide.
 - b. A colorless and odorless gas is given off.

CO_2 (Gives turbidity to lime water). Carbonate or Oxalate.
 CO (Burns with purple flame). Oxalate or compound containing Cyanogen.
 - c. A colorless gas having characteristic odor.

H_2S (Blackens lead acetate paper). Sulphide.
 SO_2 (Odor of burning sulphur). Sulphite.
 SO_2 (Odor of burning sulphur with separation of free sulphur). Thiosulphate.
 HCl (Gives white precipitate when bubbled into AgNO_3). Chloride.
 HCN (Odor of peach kernel). Cyanogen compound.
 CH_3COOH (Odor of vinegar). Acetate.
 - d. An explosion occurs.

Indicates a chlorate.

PRELIMINARY EXAMINATION

C. Mix two grams of the substance with an equal amount of anhydrous sodium carbonate, place in a cavity cut in a clean stick of charcoal and heat gradually to a high temperature with the blow-pipe.

- a. A metallic bead is formed.
 1. Soft gray bead. Pb or Cd.
 2. Hard bead. Ag, Sb, Sn or Bi.
 3. Red or yellow. Cu or Au.
 4. Hard, black, magnetic bead. Ni, Co or Fe.
- b. No metallic bead is formed.
 1. Substance yields yellow powder. Zn.
 2. Substance yields white powder, giving off brilliant white light when very hot. Ba, Sr, Ca.
 3. Substance volatilizes.
 - a. With odor of garlic and purple flame. As.
 - b. With purple flame, but no odor. Sb.
- c. Substance seems to be unchanged.

(Cool, moisten with dilute cobaltous nitrate and heat again for some minutes with blow-pipe.)

 1. Blue coloration. Al.
 2. Green coloration. Zn.
 3. Pinkish coloration. Mg.

D. Prepare a perfectly colorless borax bead by fusing on a clean platinum wire enough borax to fill a two-millimeter loop. Take up enough of the substance to cover the upper surface of the bead and heat in the colorless flame of the Bunsen burner until the bead is perfectly transparent.

Note. This bead test must not be made if a positive test was obtained with the blow-pipe. Why?

1. Blue bead indicates Co.
2. Amethyst bead indicates Mn.
3. Green bead indicates Cr.
4. Brown bead indicates Fe or Cu.
5. Gray bead indicates Ni.

E. Heat a small portion of the substance on a clean platinum wire in the colorless flame of the Bunsen burner. Note color of flame.

1. Red indicates Li or Sr.
2. Green indicates Ba, Cu or Borates.
3. Purple indicates K, or lead or silver nitrates.
4. Yellow indicates Na.

PRELIMINARY EXAMINATION

F. The Spectroscope.

The spectroscope may be used with great advantage to determine the presence or absence of Li, Na, K, Ba, Sr, and Ca. The expert would, of course, be able to detect many other metals with this instrument.

The instructor should prepare a dozen clean platinum wires by properly fusing them into the ends of glass rods. A small label should be attached to each rod and marked to indicate the metal whose salt is to be tested with this particular wire. A dozen bottles should be prepared (half dram vials), by thoroughly rinsing with distilled water and marking with clean label. These bottles should be filled as follows: two with NaCl, two with KCl, two with LiCl, two with BaCl₂, two with SrCl₂, and two with CaCl₂. One of each pair of bottles should be marked to indicate its contents, while the other should be lettered by the instructor so that he may enter in his private record, its contents. Each student should be required to record the position of the lines shown by each metal of the six above mentioned, by marking them on a chart laid off on co-ordinate paper. This is best done with colored crayons. Care must be taken to note the most important lines, and it is often well to have a standard chart for reference. The ordinary school spectroscope will show only the relative position of the important lines and not the exact position, though any given spectroscope will always show any given line at exactly the same place if the prism is not disturbed.

Having recorded the position of the important lines given by each of these metals, the student should now record the position of the lines shown by the contents of bottles which are lettered and whose contents are unknown. By comparison to the original charts, the student should be able to determine with certainty the contents of each bottle. Great care should be taken to invariably use the same platinum wire for any given bottle and to this end it is well to stand the bottle and the wire which goes with it side by side in holes bored in a wooden block.

In actual analysis the student should first make sure that the metal is in the alkali or alkali earth group. Then dissolve a small portion of the substance in concentrated HCl and test on a clean platinum wire. It is best to scrape the wire thoroughly with a knife, unless it is known to be absolutely clean.

ORGANIZATION OF DATA OBTAINED FROM THE PRELIMINARY TESTS

- a. If positive tests were obtained for any of the metals, refer at once to the solubility table, as it may be possible to shorten the list of possible acids. If positive tests for any of the acids were obtained, make a careful list of the possible metals after eliminating those shown to be absent by the preliminary tests.
- b. If negative tests were obtained for both bases and acids. Enter carefully in your notebook a list of both bases and acids not shown to be absent by the preliminary examination.
- c. The next step (on soluble salts only) may well be a test by means of sodium carbonate, for a heavy metal. If no heavy metal is indicated, test for ammonia and then make a flame or spectroscopic test for Na and K. Where no heavy metal is present, a solution of the original salt may be used for all acid tests.

FINAL DETERMINATION OF THE BASES AND ACIDS

1. THE SUBSTANCE IS A METAL OR AN ALLOY

Boil two grams of the substance with 25 c. c. of Con. HNO_3 , until all action ceases. Add a little water and filter.

Residue.

May contain the oxides of Mn, Sn or Sb; Carbon or SiO_2 .

The oxides of tin and antimony are insoluble in HNO_3 , but may be gotten into solution by the following method:

Mix the substance with five grams of a mixture of equal parts of anhydrous sodium carbonate and sulphur. Place in a porcelain crucible. Cover and heat gently at first and then over the blast lamp. Cool, extract with boiling water and filter. Acidify the filtrate with HCl and the sulphides of tin and antimony will be precipitated, if the metals were present in the original alloy. Treat this residue as directed in 10, page 4.

The oxide of Mn is brown or black and is soluble in hot HCl . This oxide may be tested directly by means of the borax bead.

Filtrate.

May contain any of the common metals. Evaporate almost to dryness and analyse for the metals as directed in 45, except that no test should be made for the ammonium radical or for ferrous iron.

2. THE SUBSTANCE IS NOT A METAL NOR AN ALLOY

A. It is soluble in water.

Analyse as directed in I, page 21.

B. It is insoluble in water, but soluble in acids.

Analyse as directed in II, page 22.

C. It is insoluble in water and acids.

Analyse as directed in III, page 22.

Note. In trying to dissolve a substance it will often be found that a portion of the substance will dissolve while some of it seems to be unaffected. It is well in this case to run an analysis on both parts of the substance, for it may be that two substances are present, one going into solution and the other not being soluble. Here two separate analyses would be much more accurate and very much easier. Where a single substance is but partially dissolved, the analysis of the dissolved portion will often disclose the fact that the salt was but difficultly soluble and thus make the analysis of the undissolved portion a simple matter.

The student may be able to analyse a mixture of several salts by noting the comparative amounts of the sample that dissolve in the various reagents and then analysing each solution separately. For instance, Barium sulphate, Zinc carbonate and Copper sulphate might be given as a single problem. The substance would appear to be a pale blue powder. Water would dissolve a portion of the substance, giving a blue solution and leaving a white powder. The residue upon treatment with HCl would be partly dissolved, leaving a white residue which would have to be boiled several times with sodium carbonate or fused before it could be analysed. Here the water soluble portion, the acid soluble portion and the insoluble portion would be analysed separately.

FINAL ANALYSIS

I. The Substance is Soluble in Water.

1. Test for NH_4 by grinding a few cubic centimeters of the liquid in a mortar with a little lime.
2. Test for ferrous iron with HCl and $\text{K}_3\text{Fe}(\text{CN})_6$.
3. Test for ferric iron with HCl and KCNS .
4. Test with litmus paper.
 - a. Solution is acid in reaction. Indicates a strong acid and a weak base or no base at all.
 - b. The solution is alkaline in reaction. Indicates a strong base and a weak acid or no acid at all.
 - c. The solution is neutral. Indicates a strong base and a strong acid or some neutral organic compound.
- d. Make a small portion of the solution alkaline with sodium carbonate.
 1. No precipitate is produced even after boiling. No metal is present other than Na , K or NH_4 , and tests for both bases and acids can be made on portions of the original substance in water solution. Test for acids as in 46, page 10, bases as in 44.
 2. A precipitate is produced with sodium carbonate. Indicates the presence of metals other than Na , K or NH_4 , and generally makes necessary the complete removal of the metal before the tests are begun to determine the acids. The metals and acids are separated as follows: Dissolve one-half of the original substance in water, make alkaline with a concentrated Na_2CO_3 solution and heat almost to boiling. Filter and test filtrate to insure complete precipitation of the metal.

Residue.

Is carbonate of the metal. Dissolve in hot dilute HCl , boil to expel CO_2 and analyse as directed in 7, page 4.

Note. In case the carbonate does not seem to be soluble in HCl , treat with HNO_3 . Evaporate to dryness, take up in water and analyse as directed in 1, page 3.

Filtrate.

Is sodium salt of the acid together with an excess of sodium carbonate.

(This solution, after proper preparation, may be examined by direct tests for the various acids which may be present. These, of course, are all acids which have not been shown to be absent by the preliminary tests.) This solution (filtrate after precipitation with sodium carbonate) will hereafter be called the PREPARED SOLUTION.

Set the prepared solution carefully away until you have completed the tests for the metals, and then refer to 46, page 10.

Before beginning analysis for the acids, read note on the use of the solubility table and data from preliminary analysis below.

USE OF SOLUBILITY TABLE AND DATA FROM PRELIMINARY TESTS.

Having completed the preliminary tests and the determination of the metals present, the student should refer to the table of solubilities and prepare a list of possible salts of the metal found, making careful note of the solubility of the original substance as found by actual trial with hot and cold water and dilute and concentrated acids. In this way the list of possible acids may be often reduced to a half dozen or less and the number of actual tests greatly reduced.

A reference should also be made at this point to the data collected in the preliminary tests, as this data is often sufficient to still further reduce the list of possible acids or to completely identify those present in the original substance.

FINAL ANALYSIS

II. Substance is Insoluble in Water (but Soluble in Acids).

Try to dissolve substance in Dil. HCl, Con. HCl, Dil. HNO₃, Con. HNO₃, and then Aqua Regia in the order given. Evaporate the solution to small volume to expel excess of acid, and neutralize with concentrated sodium carbonate solution. Boil and filter.

Residue.

Carbonate of the metal. Dissolve in HCl. Boil to expel CO₂ and treat as directed in 7, page 4.

Filtrate.

Sodium salt of the acid. Treat as directed in 46, page 19.

III. Substance is Insoluble in Water and Acids.

1. Boil three grams of the substance in a strong solution of sodium carbonate for fifteen minutes. If residue is now soluble in acids, dissolve in HCl, boil to expel CO₂, and treat for the metals as directed in 7, page 4. Treat the filtrate for the acids as directed in 46, page 19.

2. Mix two grams of the substance in a porcelain crucible with about five grams of a mixture of sodium carbonate and potassium carbonate (both anhydrous). Add one crystal of potassium nitrate and heat over the blast lamp for ten minutes or until the mass becomes inactive. As the mass cools, rotate the crucible in such a way that most of the mixture solidifies along the sides and is thus more quickly removed.

When the mixture has become cool, place the crucible in a beaker, cover with water and boil for ten to twenty minutes, or until the mass has been entirely removed from the crucible.

Residue.

Carbonate of the base, together with some of the original substance which has not been decomposed. Dissolve in HCl, boil to expel CO₂, and treat for the metals as directed in 7, page 4.

Filtrate.

Sodium salt of the acid. Treat for the acids as directed in 46, page 19.

* * * * *

INTERPRETATION OF RESULTS.

Where your results indicate the presence of two or more salts in the original sample and you are doubtful as to how any particular base was united, a study of the solubilities of the possible combinations is often sufficient to clear up the problem.

When the metal has been found, an examination of the data from the preliminary examination of the salt and a reference to the solubility table generally greatly reduce the list of acid radicals which the known facts would indicate as being possibly present.

When the number of possible acids has been reduced to a minimum, special tests should be made for each of these either on the PREPARED SOLUTION, or on the original salt. If a single test for the acid is not absolutely convincing, other additional tests should be made, followed by an examination and tests of a known sample of the salt found during the analysis.

If the substance under examination was an alloy it would, of course, contain no acid as such, but some of the acids used in dissolving it might oxidise any sulphur or phosphorus to the corresponding acids, and these elements would then best be found by the acid tests.

Likewise arsenic and chromium are often found during the analysis for the bases, when in reality they were present in the original substance as an acid.

APPENDIX

GENERAL REAGENTS.

(On desks in front of students.)

One set of **general reagents** should be provided for every two students. These reagents should be contained in glass stoppered bottles of about 250 c. c. capacity (half pint). The required general reagents are made up as follows:

Concentrated Hydrochloric Acid. Sp.G. 1.20.

Dilute Hydrochloric Acid. One part Con. HCl to 3 parts water.

Concentrated Nitric Acid. Sp.G. 1.42.

Dilute Nitric Acid. One part Con. HNO_3 to four parts water.

Concentrated Sulphuric Acid. Sp.G. 1.84.

Dilute Sulphuric Acid. One part Con. H_2SO_4 to 5 parts water.

Ammonium Hydroxide. One part NH_4OH . Sp.G. .90 to 2 parts water.

Sodium Hydroxide. 150 grams solid sticks to one liter of water.

*In preparing dilute Sulphuric acid, fill the bottles to five-sixths of their capacity with water and then add the concentrated acid.

*Sodium Hydroxide bottles should have rubber stoppers substituted for the glass stoppers, as the glass stoppers have a tendency to "Freeze" to the bottles through the formation of sodium carbonate.

Hydrogen Sulphide should be considered one of the general reagents. It is best prepared by treating Iron Sulphide (sticks) with dilute Hydrochloric or Sulphuric Acids.

The gas may be prepared in one or more "Kipp" generators (pint) which are stationed in a Hood at one end of the laboratory, or the students may make serviceable generators from large test-tubes by inserting a one-hole rubber stopper and using a glass delivery tube. (The acid should be poured away and the iron sulphide washed with water after using.) The delivery tube should always be washed carefully before using and contamination of the solution thus prevented.

Note. Some instructors prefer a solution of Hydrogen Sulphide to the gas itself. This should be a freshly prepared saturated solution. The solution has some advantages over the gas.

SPECIAL REAGENTS.

(On side shelf.)

These reagents are only occasionally used and need not be placed at the desks of the individual students.

Reagents in Solid Form.

Ammonium Chloride. Chemically Pure or Baker's Analysed.

Borax. Pure or commercially pure.

Calcium Fluoride. Commercial or pure. Powdered.

Copper Foil. Thin sheet copper. In strips one inch by one-half inch.

Ferrous Sulphate. Chemically pure. Crystals.

Iron Nails. Wrought iron. Three inch.

Litmus Paper. Red and blue in glass bottles. In short strips.

Manganese Dioxide. Purest obtainable. (Not pyrolusite.)

Potassium Chlorate. Pure crystals or powder.

Potassium Chloride. Pure crystals.

Potassium Hydroxide. Pure. Baker's Analysed. Sticks.

Potassium Nitrite. Pure crystals.

Potassium DiChromate. Pure crystals.

Potassium Nitrate. Pure crystals.

Sodium Carbonate. Pure. Or Baker's Analysed.

Sodium Nitrite. Purest obtainable.

Sodium Peroxide. Chemically pure. Baker's Analysed.

Sodium Hydroxide. Pure sticks.

APPENDIX

Liquid Reagents.

(On side shelf.)

Amyl Alcohol. The purest obtainable.

Ammonium Carbonate. To a mixture of 75 c. c. ammonium hydroxide in 500 c. c. of water, add without heating 150 gms. of the powdered salt, stir till dissolved and dilute to one liter.

Ammonium Molybdate. Dilute 100 c. c. of ammonium hydroxide. Sp.G. .90 to 250 c. c. with pure water and add 50 gms. of molybdic acid. Stir till dissolved. Dilute 250 c. c. Con. HNO_3 with 500 c. c. water and pour with constant stirring into the molybdic acid solution. Let stand over night and decant the clear liquid for use.

Acetic Acid. One part glacial acetic to four parts water.

Ammonium Oxalate. Dissolve 30 gms. of the salt in one liter water.

Ammonium Acetate. Dissolve 100 gms. of the salt in one liter water.

Ammonium Polysulphide. (Yellow Ammonium Sulphide.) Add one or two grams of flowers of sulphur to one liter of ammonium sulphide (colorless) and let stand till the sulphur is dissolved.

Ammonium Sulphide. Pass Hydrogen Sulphide gas into dilute ammonium hydroxide till solution is saturated.

Ammonium Sulphate. 100 gms. of the salt dissolved in one liter water.

Barium Chloride. Dissolve 100 gms. of the salt in one liter water.

Bromine Water. Add 10-15 c. c. bromine to one liter 10% KBr solution.

Calcium Chloride. Dissolve 50 gms. of the salt in one liter water.

Calcium Sulphate. Saturated solution.

Carbon Disulphide. (Carbon Bisulphide.) Purest obtainable.

Cobaltous Nitrate. Dissolve one gram of the salt in one liter water.

Ethyl Alcohol. (Grain Alcohol.) About 95 per cent.

Ferric Chloride. Dissolve 200 gms. of the salt in one liter water.

Ferrous Sulphate. Dissolve 2 gms. of the salt in 10 c. c. water. Solution must always be freshly prepared.

Lead Acetate. Dissolve 200 grams of the salt in one liter of water and clear with acetic acid.

Lime Water. A saturated solution of lime in water. A saturated solution of $\text{Ba}(\text{OH})_2$ is a good substitute.

Magnesia Mixture. Dissolve 110 gms. of magnesium chloride and 280 gms. of ammonium chloride in a liter of distilled water, add 260 c. c. ammonium hydroxide, Sp.g. .90 and make up to two liters.

Mercuric Chloride. Saturated solution.

Potassium Chromate. Dissolve 100 grams of the salt in one liter water.

Potassium Cyanide. Dissolve 30 grams of the salt in one liter water.

Potassium Ferrocyanide. Dissolve 100 gms. of the salt in one liter water.

Potassium Iodide. Dissolve 50 gms. of the salt in one liter water.

Potassium Permanganate. Dissolve 5 gms. of the salt in one liter water.

Potassium Thiocyanate. Dissolve 50 gms. of the salt in one liter water.

Silver Nitrate. Dissolve 25 grams of the salt in one liter water.

Sodium Ammonium Phosphate. Dissolve 75 gms. of the salt in one liter water.

Sodium Cobaltinitrite. Dissolve 100 gms. sodium nitrite in 300 c. c. water, make slightly acid with acetic acid and add 10 gms. cobalt nitrate. Let stand. Filter.

Stannous Chloride. Dissolve 50 gms. of the salt in one liter of hot dilute hydrochloric acid.

APPENDIX

THE PREPARATION OF SOLUTIONS TO BE DISPENSED AS "UNKNOWN."S.

These solutions are to be prepared by the instructor and dispensed to the students as "Unknowns" or problems. For classes of ten or more students the instructor might well prepare at least a half liter of each of these stock solutions before the beginning of the semester.

Salt used	Group	Amount in grams for 500 c. c. of solution	Remarks
Silver Nitrate.....	I	20	Distilled water.
Mercurous Nitrate.....	I	15	Clear with HNO_3 .
Lead Nitrate.....	1	15	
Mercuric Nitrate.....	II	20	Clear with HNO_3 .
Bismuth Nitrate.....	II	25	Clear with HNO_3 .
Copper Nitrate.....	II	50	
Cadmium Nitrate.....	II	30	
Sodium Arsenite.....	II	25	
Antimony Tri-chloride.....	II	20	Clear with HCl .
Stannous Chloride.....	II	20	Clear with HCl .
Aluminum Nitrate.....	III	100	Distilled water.
Chromium Nitrate.....	III	75	
Iron Nitrate (ic).....	III	75	
Nickel Nitrate.....	III	50	
Cobalt Nitrate.....	III	50	
Manganese Nitrate.....	III	50	
Zinc Nitrate.....	III	50	
Barium Nitrate.....	IV	35	
Strontium Nitrate.....	IV	25	
Calcium Nitrate.....	IV	60	
Magnesium Nitrate.....	V	100	
Potassium Nitrate.....	V	25	
Sodium Nitrate.....	V	25	
Ammonium Nitrate.....	V	40	

The above solutions will be of such concentration that approximately 100 Mg. of the metal will be contained in 5 c. c. of the solution. Thus, where only two or three unknown metals are to be found in one solution, an ordinary 20 c. c. test tube may be brought by the student to receive the solution from the stock room.

*The instructor will note a few "incompatibles," especially with metals of the first group when given with certain solutions from the second group.

APPENDIX

APPARATUS LIST.

The articles listed below will be found to answer for all the work of any ordinary course in qualitative analysis. Good work could be done with a smaller outfit.

Glass Ware.

3 Beakers.....	350 c. c.....	With lip.
2 Beakers.....	250 c. c.....	With lip.
1 Flask.....	250 c. c.....	Florence type.
1 Flask.....	500 c. c.....	Erlenmeyer type.
4 Funnels.....	3 inch.....	Long stem
12 Test-tubes.....	5x $\frac{3}{4}$ inches.....	Thin walled.
2 Test-tubes.....	5x $\frac{3}{4}$ inches.....	Hard glass.
3 Test-tubes.....	8x1 inch.....	Thin walled.
3 Ft. Glass tubing.....	5/32 inch.....	Thick walled.
1 Watch glass.....	3 inch.....	
1 Glass plate.....	3 inch.....	

Hard Ware.

1 Test-tube Brush	1 Triangular File
1 Test-tube Holder	1 Ring Stand
1 Pinch Cock	3 Rings
1 Pair Tweezers or Tongs	1 Clamp
1 Spatula	1 Bunsen Burner with Hose
1 Blow Pipe	1 Filter Stand
1 Wire Gauze, 4x4 inch	1 Pipe Stem Triangle

Other Articles.

1 Porcelain Crucible.....	10 or 15 c. c.....	With lid.
1 Porcelain Evaporating Dish.....		3 or 4 inch.
1 Box Gummed Labels.....		$\frac{1}{2}$ x1 inch.
1 Stick Charcoal.....		3 inch.
1 Length Platinum Wire.....	2 inches.....	24 gauge.
1 Package Filter Paper.....		11 centimeter.

In addition to the above articles, the student should provide himself with a towel, an oil cloth or rubber apron, a box of matches and a cake of soap, before beginning his work in qualitative analysis.

The student should begin by carefully looking over the articles in his desk and checking them on the above list. Report to the instructor all broken or defective articles.

As new articles are needed from time to time, a card should be filled out and presented to the instructor or store keeper, who will file it as a record of articles dispensed. This card should show the name of the student, the name of the article taken and the date.

SOLUBILITY TABLE

	Pb	Ag	Hg'	Sb	Sn''	Sniv	Hg''	Bi	Cu	Cd	Ni	Co	Mn	Zn	Al	Cr	Fe''	Fe'''	Pb	Sr	Ca	Mg	K	Na	NH4
Acetate.....	W	W	W	W	W	W	W	W	W	W	W	A	W	W	W	W	W	W	APR 02 1986	W	W	W	W	W	W
Arsenate.....	a	a	a	A	a	a	a	a	a	a	a	a	a	a	a	a	a	a	APR 05 1986	W	W	W	W	W	W
Arsenite.....	a	a	a	A	a	a	a	a	a	a	a	a	a	a	a	a	a	a	APR 12 1988	W	W	W	W	W	W
Borate.....	a	a	a	—	a	a	—	a	a	a	a	a	a	a	a	a	a	a	MAR 29 1988	W	W	W	W	W	W
Bromide.....	W	a	A	W	—	—	—	—	—	—	—	—	—	—	—	—	—	—	APR 08 1986	W	W	W	W	W	W
Carbonate...	A	a	a	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	APR 02 1986	W	W	W	W	W	W
Chlorate....	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	APR 08 1986	W	W	W	W	W	W
Chloride....	W	I	W _a	W _a	W	W	W	W	W	W	W	W	W	W	W	W	W	W	APR 02 1986	W	W	W	W	W	W
Chromate....	A	a	a	A	a	a	a	a	a	a	a	a	a	a	a	a	a	a	APR 02 1986	W	W	W	W	W	W
Cyanide.....	a	W _a	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	APR 02 1986	W	W	W	W	W	W
Sulfocyanide	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	APR 02 1986	W	W	W	W	W	W
Ferricyanide	W	W _a	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	APR 02 1986	W	W	W	W	W	W
Ferrocyanide	a	W _a	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	APR 02 1986	W	W	W	W	W	W
Hydroxide...	A	—	—	—	—	a	a	a	a	a	a	a	a	a	a	a	a	a	APR 02 1986	W	W	W	W	W	W
Iodide.....	a	W _a	A	W _a	W	W	W	W	W	W	W	W	W	W	W	W	W	W	APR 02 1986	W	W	W	W	W	W
Nitrate.....	W	W	W	—	W	W	—	W	W	W	W	W	W	W	W	W	W	W	APR 02 1986	W	W	W	W	W	W
Nitrite.....	W	W	—	W	W	W	—	W	W	W	W	W	W	W	W	W	W	W	APR 02 1986	W	W	W	W	W	W
Oxalate.....	a	a	a	A	a	a	a	a	a	a	a	a	a	a	a	a	a	a	APR 02 1986	W	W	W	W	W	W
Oxide.....	A	a	A	A	a	a	A	A	A	A	A	A	A	A	A	A	A	A	APR 02 1986	W	W	W	W	W	W
Phosphate...	a	a	a	A	a	a	A	a	a	a	a	a	a	a	a	a	a	a	APR 02 1986	W	W	W	W	W	W
Silicate.....	a	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	APR 02 1986	W	W	W	W	W	W
Sulfate.....	I	A	W	W _a	W	W	W	W	W	W	W	W	W	W	W	W	W	W	APR 02 1986	W	W	W	W	W	W
Sulfide.....	A	a	a	A	a	a	A	a	a	a	a	a	a	a	a	a	a	a	APR 02 1986	W	W	W	W	W	W
Sulfite.....	I	W	A	—	I	I	I	I	I	I	I	I	I	I	I	I	I	I	APR 02 1986	W	W	W	W	W	W
Thiosulfate..	W	W	W	—	W	W	—	W	W	W	W	W	W	W	W	W	W	W	APR 02 1986	W	W	W	W	W	W
Tartrate....	a	a	A	a	a	a	—	—	—	—	—	—	—	—	—	—	—	—	APR 02 1986	W	W	W	W	W	W

W=Readily Soluble in Water.

w= Sparingly Soluble in Water.

W_a=Soluble in Water, slightly acidified with HNO₃.

A=Soluble only in Concentrated Acids.

a=Soluble in Dilute Acids.

I=Insoluble in Water and Acids.

DATE DUE

APR 8 1986

MAR 2 1986

APR 12 1988

MAR 29 1988

APR 05 1986

APR 02 1986

DEMCO 38-297

